The Nature of the Ions produced by the Spraying of Water.

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INTRODUCTION.

In a paper on the electrification of water by splashing and spraying[*] the author gave a brief account of the nature of the ionisation which accompanies these processes. In a later paper[†] these results were extended. It was shown that when pure water is sprayed, ions of both signs are produced, negative being in excess. These ions are found in a certain number of distinct groups, each group having a characteristic mobility. There is no variation of mobility with time, that is to say, ions of any specified mobility will be found if an examination is made over as wide a range of time as is experimentally possible between the production and disappearance of the ionisation. The mobilities found were:—0·00038, 0·0010, 0·0043, 0·013, 0·046, 0·12, 0·24, 0·53, 1·09, 1·56, 3·27 and 6·5, all being expressed as the velocity of the ion in centimetres per second in a field of 1 volt per centimetre. As far as mobilities are concerned, no difference between the positive and the negative ions was found except that the fastest ion (mobility 6·5) was not found with a positive charge.

In an investigation of the ionisation produced by bubbling air through mercury, Prof. McClelland and P. J. Nolan[‡] found five distinct groups of ions, the mobilities of the ions in this case depending on the time elapsing from their production and also on the degree of dryness of the air. When the air was dried, or when the ions were examined as soon after formation as possible, comparatively high values of mobility were obtained. With damp air the mobilities were lower, and by increasing the time-interval between production and observation the ions could be brought to a final steady mobility. The mobilities of the five groups in this state agreed very well with the mobilities of the five slowest ions produced from water. In a joint discussion it was suggested that these five ions are the same in each case, but that when produced by the breaking up of mercury, they take some little time to add on enough water to attain to their final steady state. We imagined them therefore as water aggregates of five different

* 'Roy. Soc. Proc.,' A, vol. 90 (1914).
† 'Royal Irish Academy Proc.,' A, vol. 33, p. 9 (1916).
‡ *Ibid.*, p. 24 (1916).

sizes. In the present paper a more definite theory will be submitted as to the constitution of these ions, a theory which in the light of the fuller account which can now be given of the more mobile ions can be made to cover all the ions observed.

PART I.—DETERMINATION OF MOBILITIES OF VERY RAPID IONS.

In the previous experiments the method of observation employed was to draw the ionised air at a steady rate through a tube having a coaxial cylindrical electrode suitably insulated. The outer tube was charged to various voltages, and the current to the electrode measured. When the current-voltage graph was plotted it consisted of a number of straight lines, the intersections of the straight lines showing the voltages at which the various groups of ions were saturated. The determination of mobilities then reduces itself to the accurate drawing of the current-voltage graphs. If the observations of current are unsteady, or if the number of ions of any class is small, so that the bend due to the saturation of that class is not well marked, the possibility of an accurate determination of mobility is accordingly reduced. Great attention was given, therefore, in the previous work to the accurate drawing of these graphs. In the result it was felt that the mobilities of the different groups were fairly well established—apart from a few cases in which there appeared to be a real variation. It was felt, however, that much more information could be obtained about the more mobile ions, if a method which would more effectively separate out the different classes of ions could be employed—and especially if such a method could be devised to examine the ions as soon as possible after their production, when their numbers had not been reduced by recombination or diffusion. The method described below was found to be suitable, and it was immediately found that ions of much higher mobility than those previously observed were present. Ions which had been obscured in the other observations were readily separated out. A full account can now be given of the more mobile ions.

Experimental Method.

The apparatus used is shown in fig. 1. A strong wooden box of rectangular shape was made measuring internally 100 cm. long, 25·3 cm. wide and 14 cm. deep. To the top and bottom were fitted metal plates. The bottom plate was 50 cm. long and its end was 20 cm. from the open end of the box. This plate was supported by two metal rods passing through ebonite plugs in the bottom of the box. The plate came within 0·4 cm. of the bottom. Strips of ebonite of this thickness were placed transversely under the plate so

that its surface was quite level. Exactly above this plate were two plates
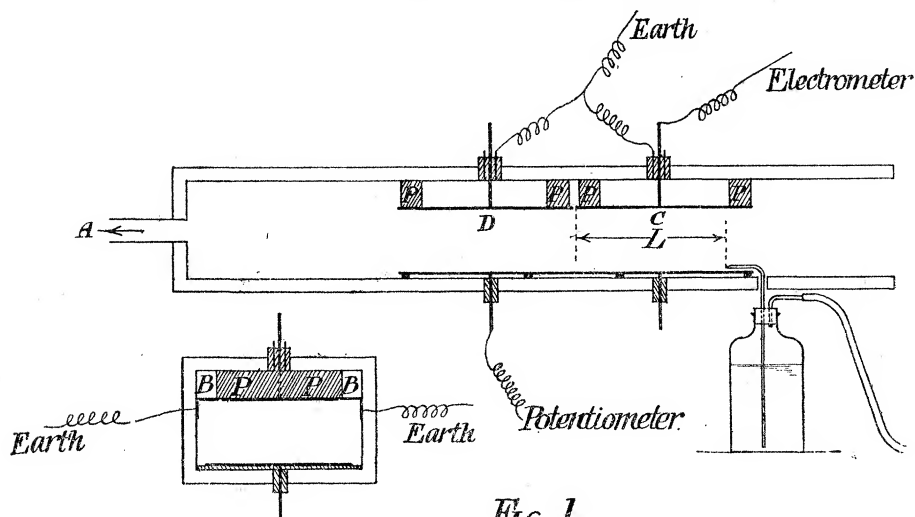C and D, each 25 cm. long, separated by an interval of about 0·2 cm. These

FIG. 1

plates were supported by metal rods passing through ebonite plugs fitted with
guard-rings connected to earth. Blocks of paraffin (P, P) served to keep the
plates in position. The lower plate was 24 cm. wide, giving a little clearance
on each side. The upper plates were 15 cm. wide. Running along on each
side of the upper plates were strips of metal 5 cm. wide (shown in end view
of apparatus). These were fastened on to wooden blocks (B, B) and were
connected to earth. There was thus a gap of 0·15 cm. at each side between
the upper plates and the earthed strips. The spraying apparatus consisted of
an ordinary metal scent-spray connected to a large glass bottle containing
distilled water. It was driven by air at a constant pressure of 27 cm. of
mercury. The nozzle of the sprayer passed through the bottom of the box
and projected a distance of 5 cm. over the lower plate. The distance
between the nozzle and the plate was approximately 0·2 cm. Connection
was made with a gasometer at A, so that a strong current of air could be
drawn through the apparatus at a uniform rate. The lower plate was
connected to a potentiometer by means of which it could be charged to any
desired voltage. In practically all the experiments the plate C was connected
to the electrometer and the plate D to earth. In a few experiments C and D
were both connected to the electrometer, but the other arrangement was
generally more suitable. The apparatus was tilted slightly so that the water
sprayed along the lower plate drained away into a vessel provided for it.

If a certain number of ions of the same mobility, u, are produced at the tip

of the sprayer, they will all move along the same path and arrive at the end of the plate C, having traversed the horizontal distance L at a voltage V, when

$$u\text{V} = \text{Q}a/\text{L}b,$$

Q being the volume of air passing between the plates per second, a being the distance between the plates, and b the inside width of the apparatus. If a current-voltage graph is plotted the following result should be obtained. From zero up to a certain voltage the plate C should receive no charge; at a certain voltage the fastest group of ions should arrive together at the plate and the graph go up steeply. It should then become level again, the current being constant while the voltage is rising until the next group of ions is received. The graph will then resemble a series of steps, each step representing the collection of a group of ions of a certain mobility. The mobilities are readily calculated from the voltage at which the step occurs by the formula given above. It is obvious that if this can be realised in practice, the method is much easier and more accurate than that previously employed for the determination of mobilities. It has the special advantage also that it separates out ions of mobilities lying close together and makes it possible to obtain a good value of mobility for each.

When the method was put into practice the step-like nature of the current-
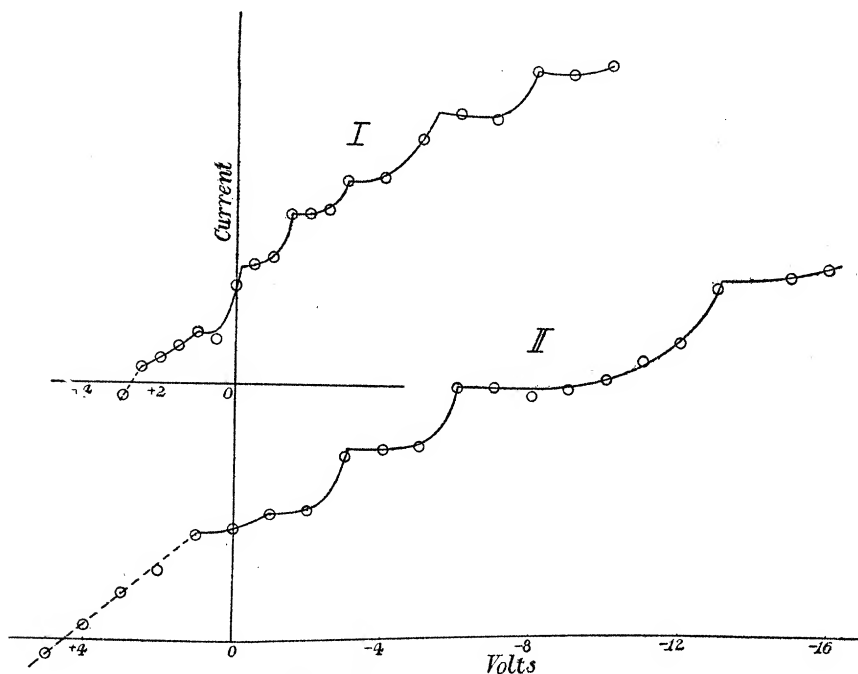

Fig. 2

voltage graphs was at once apparent. But an unexpected complication had
arisen which will be clear from an inspection of fig. 2. These two graphs deal
with negative ions. The steps are very well developed, but in each case for
zero voltage a very considerable negative current is recorded. Positive
voltages, in one case three, and in the other case over four volts, have to be
applied in order to bring the negative current down to zero. Independently
of the applied voltage there seems to be a negative field in operation of the
order of three or four volts. A little consideration makes the origin of this
field clear. The jet from the sprayer contains (see previous paper*) minute
water drops with a high positive charge and large numbers of positive and
negative ions with mobilities of all values from very fast to very slow. The
negative ions are in excess, the difference corresponding to the positive charge
on the water. When this jet is spread out over the lower plate a certain
fraction of the water-drops are caught by the plate and give up their charge
to it. A commensurate number of ions will not be discharged, because,
whereas the water drops may be carried against the plate by the velocity
of their projection from the sprayer, the ions will not retain such a velocity,
but will take up almost at once the stream-like motion of the air in the
apparatus. The result is that an excess of negative electricity is formed close
to the lower plate. In this way a field could easily be set up of the order of
magnitude observed. The distance between the plates is approximately
10 cm. The positive voltage necessary to secure a zero reading of current
varied between zero and 6 volts, but was generally about two. These
variations occurred in such a way as to lend support to the explanation just
given. Slight variations in the position of the spraying nozzle would mean
that more or less of the water-drops would be discharged against the lower
plate. It was found that the field varied accordingly. Again, if the velocity
of the air in the apparatus is increased, it is to be expected that the negative
excess present at any time would be diminished and that the field would be
correspondingly smaller. It is found that the field does vary in this way with
the air-velocity.

It is very important to be clear as to how far this phenomenon affects the
determination of mobilities. In practically all the experiments dealt with
here the rate of drawing air through the apparatus was such that Vu
(saturation voltage × mobility) had the value 47·0. The voltage corre-
sponding to the determination of the mobility of the ordinary small ion
would be between 25 and 30. As the value of the extra voltage was
generally two, and sometimes less, it was easy to choose conditions so that the
effect is negligible for the small ion and for any ion of lower mobility. It is

* 'Roy. Soc. Proc.,' A, vol. 90 (1914).

in connection with the fast ions, and especially with the very fast ones, that the effect is most important. The question is this : Can we treat this field as being equivalent to a uniform steady field, which is simply to be added on to the applied field if the latter is negative, or subtracted from it if it is positive ? It is easy to verify that, for any fixed position of the spraying nozzle and for a uniform air-blast, the voltage necessary to give zero current is quite constant, so that the field is steady in that respect at least. It will not be affected either by the different motion of the ions under different applied fields, because the small voltages used in dealing with the very mobile ions leave the motion of the great majority of the ions absolutely unaffected. The voltage to be added or subtracted will not therefore be different for different values of the applied field. As to whether the field is sufficiently uniform to be treated simply in an additive way, we can look to experimental results for guidance. Observations of the current-voltage curve have been obtained under various conditions, the " correcting voltage " or positive voltage necessary to give zero current varying between zero and 4·5. The observations when the correcting voltage was zero are especially valuable. The Table given below contains the results of these observations ; it shows the voltage at which steps occurred on the current-voltage curve—these voltages having been corrected by the addition of the correcting voltage. These observations deal with negative ions.

Table I.

Correcting voltage.	Voltages at which steps occur (corrected).					
0·0	1·7	—	—	5·75	—	9·5
2·8	1·8	2·9	4·3	5·8	8·2	10·8
3·75	1·75	3·35	—	—	—	—
4·5	—	3·5	—	5·5	7·5	10·5

This Table deals with some of the steps corresponding to the very rapid ions. It is clear that the corrected voltages agree very well among themselves, and that they agree very well with the voltages observed in the case when no correction had to be applied In every series of observations, consequently, whatever part of the current-voltage curve is being examined, it is necessary to take a few observations with low positive voltages, in order to determine the point at which the graph crosses the line of zero current. It is much easier to proceed in this way than to endeavour to arrange the apparatus so that the correcting voltage it always zero. Efforts were directed to keeping the necessary correcting voltage as low as possible, and to determining its value accurately for each experiment.

An interesting example of this determination is given (III, fig. 3). As the curve is drawn, the voltage corresponding to zero current is $+3\cdot75$.
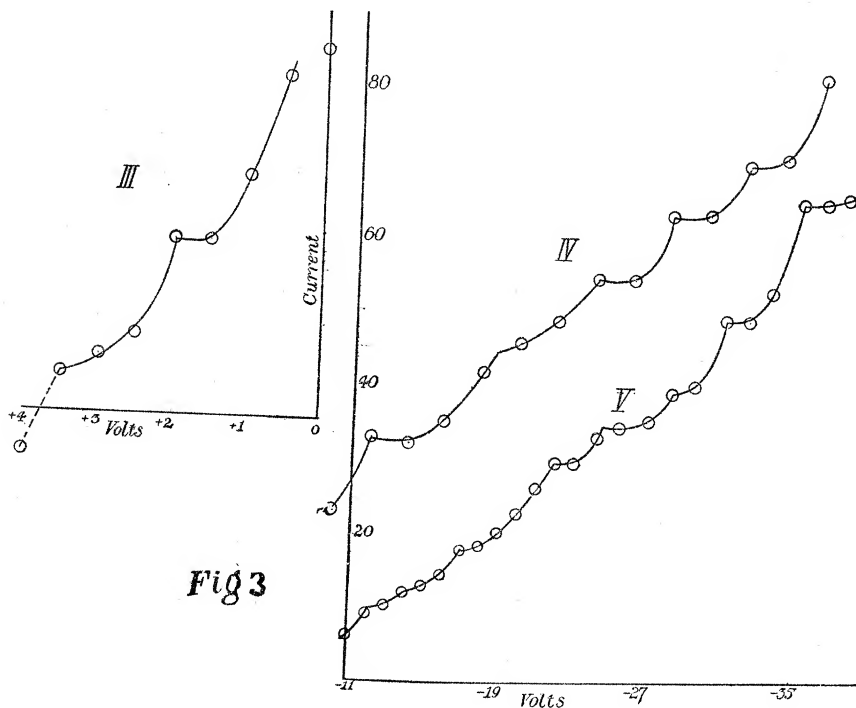

Fig 3

Taking this as the correct zero of voltage, we see that the first well marked step is at $1\cdot75$ volts. But, before that, there seems to be an abrupt rise between zero and $0\cdot25$ volt. Under the conditions of the experiment, Vu being $47\cdot0$, the mobility of the ion corresponding to this step would be $47/0\cdot25 = 188$ cm./sec., or some higher value. The same indications are present in curve I (fig. 2), but the curve just mentioned is the best example, as the readings of current were big and steady. We can only attribute this effect to the presence of free electrons. There are no corresponding indications on the positive curves. The point is worthy of fuller examination.

Two examples are given (IV and V, fig. 3) of the graphs obtained with higher values of voltage. Both refer to negative ions. The voltages have been corrected.

The five curves given were obtained under the same conditions as regards air-velocity, etc.; the value of Vu is consequently the same for all, and they are therefore strictly comparable with one another. A consideration of the curves will illustrate some points in connection with these experiments. Thus, if we compare I and II, we find that they agree in giving steps of

current at (corrected) voltages of approximately 6, 8, and 11. They also agree in giving a step at a voltage of about 3, but curve I shows steps at 1·8 and 4·3 volts, which do not appear in curve II. An explanation can be found in the fact that sufficient observations at various voltages were not taken in the second instance, and that the steps in the curve were thus obscured. In the case of curve I, observations were taken at intervals of half a volt over this part of the curve, whereas the intervals in curve II are double this value.

If we compare curves IV and V, we find that they agree in giving steps at 12, 24, 28 and 31 approximately, but that between 12 and 24 they are in disagreement, curve V showing steps which do not appear on curve IV. One of these steps—that at 14 volts—is very faintly marked ; in fact, there is hardly any justification for indicating a step at this point except that it shows up more strongly in other curves. And again both of these curves are in disagreement with curve II, which gives no indication of a step at 12 volts. Part of this disagreement may be attributed as before to the fact that if observations are not taken close enough together steps may be obscured. But in addition there appears to be over part of the curve, say from 10 to 24 volts, some unsteadiness or variation which prevents a consistent agreement. Most of the steps on the current-voltage curves are found easily and are always present. In this particular region some have been established fairly well, but others must be regarded as in some degree open to doubt. The latter are specially noted later.

In the actual determinations of mobility, shorter curves than those illustrated were generally used, the observations being taken close together round about the regions in which steps were indicated in preliminary surveys.

Statement of Results.

The following Tables give the values of mobility of the ions deduced from the best observations. Only ions of mobility greater than unity have been included ; those of lower mobility have not yet been so fully examined by this method.

Comparing the positive and negative ions we find that the fastest positive and the second fastest negative are practically the same. After that there is disagreement, but the six slowest in each case are practically identical.

Table IIA.—Negative Ions.

Mobility.	Remarks.
27·0	
15·2	
11·4	Observed three times. Not well marked.
8·34	
6·06	
(4·42) }	It is not quite certain whether these mobilities represent different ions
3·83 }	or different observations of the same ion. Two observations of 4·42.
2·69	
2·28	Two observations.
1·94	
1·70	
1·49	
1·34	
(1·15)	Sometimes absent.
1·06	

Table IIB.—Positive Ions.

Mobility.	Remarks.
15·5	One observation.
4·86	
3·43	
2·76	
2·42	One observation.
1·93	
1·72	
1·56	
1·37	
(1·18)	Not well marked.
1·05	

Possible Sources of Error.

Some of the mobilities are much higher than would be anticipated.   It would be useful at this stage to see if this could be due to any error in the method of working.   In estimating mobilities by the formula $u\mathrm{V} = \mathrm{Q}a/\mathrm{L}b$ certain assumptions have been made.

1. It was assumed that all the ions are produced at the tip of the sprayer. It is possible that the ions are not all produced at one point, or that, if they are, that point is not the tip of the sprayer.   But the fact that the steps in the current-voltage graph are so steep and sharply marked is a pretty clear indication that the origin of the ions is sharply localised, at least within the limits of experimental observation.   It might be said, however, that the point at which the ions are produced is not the tip of the sprayer but some point 2, 3 or 4 cm. in front of it.   This is very unlikely, and if it were true it would mean that our estimate of L is too high and that the true values of mobility are higher than those given above.

2. The quantity Q was estimated by measuring the total quantity of air passing between the upper and the lower plates per second. But the origin of the ions was some distance (0·2 cm.) above the lower plate. Therefore the quantity Q is not the total volume of air, but is less than it by an amount equal to the quantity of air flowing between the lower plate and a plane drawn parallel to it through the tip of the sprayer. But it is easily seen that if the air velocity at the plates is zero, and if the distribution of velocities between the plates is approximately parabolic, the error involved in this estimation is altogether negligible, when the distance between the plates is as great as 10 cm.

3. The disturbing effects of the rush of air from the spray were neglected. But if this rush of air had any effect on the ions it would mean that the ions were carried along with a certain velocity parallel to the bottom plate instead of partaking of the undisturbed stream-line motion of the air. This would mean that a higher voltage than is allowed for in our calculation would be necessary to bring them over to the upper plate, and that consequently the values for mobility are too low. It is very unlikely, however, that there is any effect of this kind. When an ion is produced at the tip of the sprayer it comes under the influence of the field and at once moves up out of the rush from the sprayer and takes up the velocity of the layers of air into which it successively moves.

4. The principal assumption is in connection with the " correcting voltages." This has been discussed already, but perhaps two points may be emphasised once more. The first is that our values for the mobilities from, say, mobility = 2 downwards, are practically unaffected by any uncertainty that might be felt in this connection. The second point is that the values deduced from the experiment in which no correcting voltage had to be applied do not disagree in any way with those deduced from other experiments.

The facility with which mobilities can be determined by this method is clear from an inspection of the graphs. There are a few other points about the method which are worthy of note.

Each group of ions travels along a path of its own through air free from any other ions. Thus there is no loss by recombination, and no complication introduced by encounters with other ions. Again, if any member of the group changes in mobility, say by an increase of mass, it drops out of the group and follows a different path for the rest of the way. The unchanged ions arrive at the upper plate together, causing an abrupt upward step in the curve. The ions which have increased in mass arrive at various higher voltages, and their effect on the curve is to give a slight upward slope to the approximately horizontal part between steps. This effect

is very marked in the part of the positive curves corresponding to high mobilities. The conclusion is that the very small positive ions are varying in a more rapid way than has been noticed in the case of the negative ions. The very well-marked steps in the negative curves show that in this case there is little variation of mobility during the time of experiment. The values of mobility deduced from the curves are therefore the true mobilities of ions observed at their formation and undergoing no change during the process of observation.

A general study of the curves shows that it is the fastest ions and then the slower ones from 1·94 to 1·06 which give the sharpest steps. The conclusion is that these ions have a fair degree of stability and a definite period of existence. The ions, on the other hand, of mobilities between 4·4 and 2·28 do not give indications that are so satisfactory or consistent. It is probable then that these ions are of a more fugitive character.

Before we endeavour to arrive at an idea of the nature of these rapid ions, it is convenient to consider the ions of low mobility which are formed at the same time. From a preliminary study of the slower ions we can derive some suggestions as to the magnitudes involved in the case of the ions which have just been described.

PART II.—THE NATURE OF THE LARGER IONS PRODUCED FROM WATER.

In the introduction to this paper an account has been given of the variety of slowly moving ions produced when distilled water is sprayed. The five slowest ions have mobilities respectively, 0·00038, 0·0010, 0·0043, 0·013 and 0·046. It will hardly be disputed that they are composed of water. The circumstances of their production, the way in which their growth depends on time and on the moisture of the air when, as in the experiments of McClelland and P. J. Nolan, they are not produced directly from water, all lend support to this idea, which from any point of view seems to be the only feasible one. Assuming, then, that they consist of water, there are two ways in which we can calculate their size, (1) by applying Stokes' Law, and (2) by using the theoretical formulæ deduced for the mobility of an ion which is great in comparison with the molecules of the gas which contain it.

Application of Stokes' Law.

The modified form of Stokes' Law which follows was deduced by Millikan[*] from observations on the fall of minute oil-drops in air

$$v = \frac{2}{9} \frac{ga^2(\sigma - \rho)}{\eta} \left\{ 1 + \frac{l}{a} \left(0{\cdot}874 + 0{\cdot}32\, e^{-1{\cdot}54a/l} \right) \right\},$$

[*] Millikan, 'Phys. Rev.,' vol. 1 (1913).

where l is the mean free path of the gas molecules. Substituting for g the acceleration Xe/m due to an electric field of intensity X, e being the charge on the ion, and assuming for the present that the charge is the electronic charge 4.77×10^{-10} electrostatic units, we can calculate the radius of these five ions. For η the value 0.000182 is taken, and for l the value 9.27×10^{-6} cm. The values deduced are tabulated below.

Table III.

Mobility.	Calculated radius.	Mass.	Ratio of masses.
	cm.	grm.	
0·00038	4.08×10^{-6}	2850×10^{-17}	1770
0·0010	2·41	587	365
0·0043	1·12	58·7	36·5
0·013	0·637	10·8	6·7
0·046	0·337	1·61	1

The masses of the ions calculated in this way are related to one another in a very definite way. If we exclude the second ion, there is an almost uniform ratio between the masses. The value of this ratio is about 6·5. The special reason for excluding the second ion will be dealt with at a later stage.

The validity of Millikan's formula for drops of very small radius might be questioned. We can show, however, that the results deduced are in close agreement with those deduced from theoretical formulæ for the mobility of ions.

Application of Mobility Formulæ.

Sir J. J. Thomson,[*] on the assumption that the effects of collisions between ions and molecules are the same as those between two hard elastic spheres, gives the formula

$$\text{Mobility} = \frac{e}{N\pi\sigma^2\sqrt{M \cdot \Omega}} \left\{ \frac{M_1+M_2}{M_1M_2} \right\}^{\frac{1}{2}} \frac{5}{4} \left\{ \frac{M_2+3M_1}{M_2+5M_1} \right\},$$

where N is the number of molecules of the gas per unit volume, M the mass of a hydrogen molecule, Ω its average velocity at the temperature of the gas, M_1 the mass of the ion, M_2 that of a molecule, σ the sum of the radii of an ion and a molecule, and e the charge on an ion. If the mass of the ion is large compared with that of the gas molecule this becomes

$$\text{Mobility} = \frac{e}{N\pi\sigma^2\sqrt{M \cdot \Omega}} \frac{3}{4} \sqrt{\frac{1}{M_2}}.$$

[*] Sir J. J. Thomson, 'Phys. Soc. Proc.,' Part I, vol. 27 (1914).

On the same supposition with regard to elastic collisions, Townsend,[*] follow-
ing Langevin's[†] investigation of the coefficient of interdiffusion of two gases,
gives for the velocity U of an ion in the direction of an electric force X the
formula

$$U = \frac{3\,e\mathrm{X}}{8\,\sigma^2\mathrm{N}} \sqrt{\left(\frac{h\,(\mathrm{M}_1+\mathrm{M}_2)}{\pi\,\mathrm{M}_1\mathrm{M}_2}\right)},$$

where $2h = \mathrm{N}/\Pi$, Π being the pressure of a gas containing N molecules per
cubic centimetre.   When the mass of the ion is large compared with that of
the gas molecule, this becomes identical with the corresponding formula of
Sir J. J. Thomson.

Using this formula, then, we can find the value of σ corresponding to the
various ions.   Assuming once more that the charge is the unit electronic
charge, we find for the radius of the ion of mobility 0·00038, the value
$4\cdot16 \times 10^{-6}$ cm. as compared with the value $4\cdot08 \times 10^{-6}$ cm. deduced from
Millikan's formula.   The agreement between the two values is remarkably
good.

But a serious difficulty arises at this stage.   If the large ion has the size
which these two very different methods of calculation agree in ascribing to it,
it should be very easily visible in the ultramicroscope.   But de Broglie[‡]
states that the large ion produced from flames cannot be seen in the ultra-
microscope, and suggests that it consists of some sort of loose grouping too
diffuse to give an ultramicroscopic image.   We have considered each ion so
far as if it could be represented as a spherical globule of water.   We must
recognise that this is a very definite assumption and that the alternative
possibility must be considered, namely, that some at least of the ions consist
of loose aggregates of some smaller drops which have not coalesced.

This possibility can be considered more effectively at a later stage, for even
if we at once accept de Broglie's experiment as decisive and regard the largest
ion as a grouping of something smaller, we have as yet no clue to what that
smaller globule may be, nor have we as yet any evidence as to how many of
the ions are built up in this loose manner.   When we arrive at the stage at
which the ions are compact spheres of different sizes the formulæ we have
used will then be valid.   Meanwhile we will continue the calculations based
upon the original assumption which regards all the ions as consisting of
compact aggregates of water.

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* Townsend, 'Electricity in Gases,' p. 81 (1915).
† Langevin, 'Ann. de Chim. et de Phys.' (8), vol. 5, p. 245 (1905).
‡ De Broglie, 'Comptes Rendus,' vol. 148, p. 1317 (1909).

Sizes of Ions Treated as Drops Calculated from Mobility Formula.

The theoretical formula for mobility may be put in the form

$$\text{Mobility} = \text{constant}/a^2,$$

where a is the radius of the ion. In the case of the first five ions the average ratio of mobility of each ion to the next slowest is 3·3. Therefore the radii of the ions are in the ratio $1 : \sqrt{3\cdot3}$ and their masses are in the ratio $1 : (3\cdot3)^{3/2}$, which is approximately $1 : 6$. The values deduced from Millikan's formula have already suggested that the masses of the ions are related to one another in a ratio almost identical with this. Assuming then that the ions are built up in this way, each ion having a mass six times that of the next smallest, we can calculate the mobilities of the ions starting from the slowest. The mobility of each ion is got from the next slowest by multiplying by $6^{2/3}$, which is equal to 3·302. The following Table shows the calculated mobilities compared with those experimentally found. The agreement is very good except in the case of the second ion.

Table IV.

Observed mobility.	Calculated mobility.	Mass.
		grm.
0·00038	(0·00038)	$\frac{4}{3}\pi\,(4\cdot16 \times 10^{-6})^3 = 3\cdot02 \times 10^{-16} = m$
0·0010	0·00129	$m/6$
0·0043	0·0043	$m/6^2$
0·013	0·014	$m/6^3$
0·046	0·047	$m/6^4$

The ions next in order had the mobilities 0·12, 0·24, 0·53, and 1·09. The ratio of mobilities is now different. The value of $0\cdot12/0\cdot046$ is about 2·6, and the subsequent ratios have values approximately 2. If the ratio of the masses of the ions was 3, the ratio of the mobilities would be $3^{2/3} = 2\cdot08$. This agrees very well with the ratio found for the faster ions, but the value 2·6 found for one ratio is in disagreement. The latter value suggests a mass ratio of 4, which would give a ratio of mobilities of the value of $4^{2/3} = 2\cdot52$. It is possible that the ratio of the masses of the ions is uniformly 3 and that the disagreement is in part due to experimental error and in part to the imperfection of our theory. For the moment, however, we will assume that the slowest ion has a mass one-fourth that of the last ion in the Table above and that the succeeding ions have masses in the ratio of 3. Calculating the values of the mobilities on these assumptions, we find that they correspond very closely with the experimental values.

Table IVA.

Observed mobility.	Calculated mobility.	Mass.
0·12	0·12	$m/6^4 \times 4$
0·24	0·24	$m/6^4 \times 4 \times 3$
0·53	0·51	$m/6^4 \times 4 \times 3^2$
1·09	1·06	$m/6^4 \times 4 \times 3^3$

Possibility of Multiple Charges.

These calculations rest on the assumption that the charge on each of these ions is the unit electronic charge. Kennedy[*] has shown, however, that the large ions produced from flames may have various charges, e, $2e$, etc., up to at least $6e$. We are obliged, therefore, to consider the possibility that here also multiple charges are present. In that case we should expect to find a mixture of ions of charges e, $2e$, and $3e$, etc., with certain charges predominating. Kennedy's results support this view. In the case of ions as large as those with which we are dealing, there is no theoretical justification whatever for the idea that the size could depend *ceteris paribus* on the charge. Therefore, on any theory of mobility, we should expect to find a $1:2:3:4:\ldots$ relationship between the observed mobilities of the ions. But no such relationship is apparent from an inspection of the mobilities obtained. It is most unlikely, therefore, that the majority of the ions have other than single charges. There remains the case of the second ion. A great many observations of this ion gave the value 0·00088, other readings varied from that up to 0·00131. The last value would agree with that calculated, 0·00129 (see Table IV), and with the value observed by McClelland and P. J. Nolan, 0·0013. It was noted also in the previous work that the determination of the mobility of the final ion was difficult. The observations varied from 0·00031 to 0·00044, and on some occasions it was difficult to decide whether this ion was present at all. Again, very good observations were obtained of ions of mobility 0·00065, which could not be made to fit into any group. It is clear, then, that in the case of the two slowest ions, we have a variety of values which might be accounted for by the existence of multiple charges.

On the whole, however, the assumption that the charge on the ions is the electronic charge is justified.

We arrive, then, at the idea that when pure water is broken up, water aggregates of certain definite sizes are produced. These have at least a

* Kennedy, 'Roy. Irish Academy Proc.,' A, vol. 33, p. 58 (1916).

certain degree of stability, and, on our present hypothesis, their masses are related to one another, first in a ratio of 6, and then for the faster ions in a ratio of 3. But intervening there is a step from the ion of mobility 0·047 to the ion of mobility 0·12, where we have supposed a mass-relationship of 4. It is possible, of course, that the true ratio of the masses of the ions is 3 : 1, in harmony with the other lighter ions; in that case the calculated mobilities of the faster ions would have to be lowered about 20 per cent. This would involve a disagreement of about that magnitude between the calculated and the observed values. Such a disagreement would not be very serious, seeing that any error in calculation due to the inadequacy of the theory is cumulative in the method which we have employed.

The ion of mobility 0·047 seems to occupy a special position. There are reasons for believing that it is a particularly stable aggregate. Taking the radius of the largest ion (mobility 0·00038) as $4·16 \times 10^{-6}$ cm., the radius of this ion will be

$$4·16 \times 10^{-6}/6^{4/3} = 3·8 \times 10^{-7} \text{ cm. approximately.}$$

Now, it has been shown by Sir J. J. Thomson[*] and Langevin,[†] that drops of a certain radius should have a very high degree of stability. The value of the radius of such a drop is calculated as 5×10^{-7} cm. This is in rough correspondence with the value that has been found above, and it is possible, therefore, that the ion of mobility 0·047 is the true persistent ion deduced by Sir J. J. Thomson and Langevin rather than the ordinary "large ion," the radius of which we have shown to be $4·16 \times 10^{-6}$ cm. or larger.

The Larger Ions Considered as Loose Groupings.

In discussing the larger ions as loose assemblages of some smaller unit rather than as compact masses, we must make some assumption as to the nature of the unit. This unit we may assume to be the largest possible single water-globule, the true "persistent ion" of Langevin and Sir J. J. Thomson, which we have just suggested is identical with the ion of mobility 0·047. The next largest ion, instead of being formed from six of the latter, coalescing into a larger water-sphere, as we supposed before, is, on the present view, formed from a loose group of three. The viscous resistance to motion offered by this group of three will probably be something greater than three times the resistance of each of the drops from which it is formed, corresponding with the observed ratio of the mobilities of 3·3. Hence we might regard the ions of mobility 0·013, 0·0043, 0·0013,

[*] 'Conduction of Electricity through Gases,' p. 149 (1903).
[†] See Chauveau, 'Le Radium,' March–April, 1912.

and 0·00038 as loose groups of 3, 9, 27, and 81 water-globules of the stable size. The ions with mobilities intermediate between these which have been observed by McClelland and P. J. Nolan in dried air would be built up in the same way from a smaller unit. This is only a slightly more definite statement of the theory put forward by Prof. McClelland and P. J. Nolan, and the present author in the previous paper already referred to.

The masses and dimensions calculated above for the faster ions would remain unaltered in the new arrangement. The new scheme has this advantage, that it is easier to see why all the ions have, in general, unit charge. Each ion is formed from three smaller ones, which will in general be two positives and a negative, or two negatives and a positive. We can also easily provide for the formation of ions carrying a number of charges, the mobility of which will not be sensibly different from that of the ion with unit charge. For supposing that two, three, four or any higher number of the latter ions, all of the same sign, come together to form a loose grouping, the resistance of the system will be increased in approximately the same proportion as the charge, so that the mobility will be very much the same as that of the singly charged ion.

There are thus two possible views of the larger ions; that which regards them as single water-globules and that which looks on them as groupings of a smaller drop, which is the real stable water drop. There is no doubt that the ultra-microscopic experiments of de Broglie on flame gases give a very strong support to the second view. The greater regularity in the process of building up of ions which it permits and the ease with which it explains multiple charges are also strongly in its favour. Further experiments on the large ions should put the matter beyond doubt. Meanwhile our calculations for the smaller ions are still valid.

Before considering the very rapid ions it is of interest to calculate the size of the smallest of the ions which we are considering at present. This ion, of observed mobility 1·09, has a mass (Table IV) $= m/6^4 \times 4 \times 3^3$, where $m = 3·02 \times 10^{-16}$ grm., calculating on the basis of Sir J. J. Thomson's formula. Thus the mass of the ion is $2·14 \times 10^{-21}$ grm. The mass of a molecule of water is 3×10^{-23} grm.; therefore this ion contains $214/3 = 71$ molecules of water. If we take the value deduced from Millikan's formula we find that the corresponding result is 66 molecules of water.

Part III.—The Nature of the Smaller Ions Produced from Water.

When we consider the values obtained for the mobilities of the smaller ions we are confronted with mobilities which are unexpectedly high. There are two ways in which we might try to make these mobilities fit in with normal

values: (1) We might suppose, at least in the case of the negative ion, that what we are dealing with is an electron which has become attached to a molecule or group of molecules for a certain portion of its path, or (2) we might suppose that there are present ions with a variety of multiple charges. On the first hypothesis, it is very difficult to imagine how a variety of high mobilities sharply differentiated from one another could be produced. But, apart from that, the fact that we find a positive ion with mobility 15·5 shows that we have to deal with molecules. The question of multiple charges is not so easily decided. If there were molecules present with one, two, three charges, etc., we would expect to find a 1 : 2 : 3 : 4 : ... relation between the mobilities. An inspection of the table of mobilities shows that it is easy enough to pick out here and there mobilities which are roughly in the ratio 1 : 2 or 1 : 3 but we can find no sustained 1 : 2 : 3 : 4 : ... relation. The first three well-established mobilities, 27, 15·2 and 8·34, may suggest 3 : 2 : 1. But the numerical agreement is not sufficiently good. Even if we admitted that these ions had three, two and one charges respectively, we have to explain why the doubly charged positive ion (mobility 15·5) occurs while there is no trace of this ion with a single positive charge.

Any such allocation of multiple charges, moreover, does not make much change in the difficulty as regards high values of mobility. For example, even if the 3 : 2 : 1 ratio of charges mentioned above could be successfully established, it would leave us with a singly charged ion of the unusually high mobility of 8·34.

Calculation of the Mobility of an Ion.

The very high values of mobility obtained in the present work seem to support the view that the collisions between ions and molecules may be regarded as taking place between hard elastic spheres. The other hypotheses as to ionic collision made familiar by the work of Wellisch[*] and Sutherland[†] would yield much lower values.

On the elastic collision hypothesis Sir J. J. Thomson,[‡] finds for the mobility of an ion the equations

$$R = \frac{e}{N\pi\sigma^2\sqrt{M \cdot \Omega}} \left(\frac{M_1 + M_2}{M_1 M_2}\right)^{\frac{1}{2}} \frac{5}{4} \left(\frac{M_2 + 3M_1}{M_2 + 5M_1}\right)$$

and

$$R = \frac{e}{N\pi\sigma^2\sqrt{M \cdot \Omega}} \left(\frac{M_1 + M_2}{M_1 M_2}\right)^{\frac{1}{2}} \frac{5M_2(M_1 + 3M_2)}{15M_2^2 + 10M_1M_2 - M_1^2}[§]$$

according as M_1 is greater or less than M_2. N is the number of molecules of

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[*] Wellisch, 'Phil. Trans.,' A, vol. 209, p. 272 (1909).

[†] Sutherland, 'Phil. Mag.,' Sept., 1909.

[‡] 'Phys. Soc. Proc.,' Part I, vol. 27 (1914).

[§] There is a misprint in this formula as published.

the gas per c.c., M the mass of a hydrogen molecule, Ω its average velocity at the temperature of the gas, M_1 the mass of the ion and M_2 that of the molecule. We have already used the formula for the case when M_1 is large compared with M_2. We can use these formulæ for calculating the mobilities of various possible aggregates of molecules, but two difficulties arise. The diameter of the sphere of influence of a molecule is not known accurately, and even if we could assign a value to σ in the case where the ion is a single molecule, we can only endeavour to approximate to it when the ion is a cluster of several molecules.

As the agreement between Sutherland's values of σ for the ordinary gases and those deduced from the limiting density is very good, it was decided to rely upon these two methods of calculation. The values $2\cdot9 \times 10^{-8}$ cm. for air and $3\cdot45 \times 10^{-8}$ cm. for water have therefore been used in deducing the mobilities of various possible ions. In calculating the mobility of a composite ion formed by n molecules of a gas, the diameter of the molecules being s_1, in a gas of which the molecules had diameter s_2, the formula $\sigma = \frac{1}{2}(s_2 + n^{\frac{1}{3}}s_1)$ has been employed.

As to the composition of the ions, two possibilities present themselves— they may be aggregates of air-molecules (making no distinction for the moment between oxygen and nitrogen) or they may be aggregates of water. The balance of probabilities is altogether in favour of the latter view. The slowest of these fast ions (mobility $1\cdot06$) is identical with the ion which was considered to consist of a cluster of about 70 water-molecules. From that ion up to the fastest there are a variety of ions increasing in mobility and therefore decreasing in size. There is no indication of any transition where the ions cease to be of water and begin to be composed of air. There is no special reason in these experiments why a greater number of groupings of air-molecules should be formed; whereas there is very good reason to expect all possible aggregations of water. Further reasons in support of this view will be brought forward at a later stage in this paper.

Assuming then that we are concerned altogether with ions composed of water, we can employ the formulæ given by Sir J. J. Thomson to calculate the mobility of ions composed of 1, 2, 3, and various higher numbers of water-molecules. In the following Table mobilities calculated for various groupings of water-molecules are given together with the mobilities observed, negative and positive.

Table V.

Number of H₂O molecules.	Calculated mobility.	Observed mobility.	
		Negative.	Positive.
1	12·3	15·2	15·5
2	7·40	8·34	—
3	5·66	6·06	—
4	4·70	—	4·86
6	3·67	3·83	—
7	3·36	—	3·43
12	2·49	2·69	2·76
(15)	2·17	(2·28)	(2·42)
18	1·97	1·94	1·93
24	1·72	1·70	1·72
30	1·53	1·49	1·56
36	1·31	1·34	1·37
48	1·14	(1·15)	(1·18)
54	1·04	1·06	1·05

Comparison of Calculated with Experimental Values of Mobility.

The mobility calculated for an ion consisting of one water-molecule with unit charge (12·3) is in fair agreement with the values 15·2 and 15·5 found for negative and positive ions respectively. A water-molecule with two charges would have a mobility 24·6, according to our calculations. This corresponds fairly well with the fastest ion observed (mobility 27). No place has been found in the above Table for the ion sometimes observed, the mobility of which was 11·4. If the ion consisting of three water-molecules had a double charge, its mobility should be 11·3. This is the most probable explanation of this ion. The values for mobility of the negative ions fit in fairly well with the values calculated for ions consisting of 2, 3, 6 and 12 water-molecules, with a tendency for the observed values to be higher than the calculated ones; the agreement for 18, 24, 30, 36, 48 and 54 is very good, both for positive and negative. Of course, in the last two cases, a fairly big change could be made in the number of water-molecules without very seriously affecting the mobility; but the way in which the observed values agree with those calculated for even increments of 6 water-molecules from 18 to 36 is very striking. With regard to the ions of 12 and 15 water-molecules, it is possible that in this case we are really only concerned with one ion consisting of 12 rather than 15 molecules. There are only two negative observations giving the value 2·28, and one positive giving the value 2·42. Perhaps the disturbing element is one of the slower ions with a double charge. If we eliminate the ion of 15 molecules, then the negative ions go fairly evenly 1, 2, 3, 6, 12, 18, 24, 30, 36,

48 and 54.   In the case of the positive ions nothing was found corresponding to the ions of 2 and 3 water-molecules.   The next highest mobilities after that which we suppose to be due to one molecule do not agree with any values found in the case of negative ions.   These mobilities (4·86 and 3·43) are deduced from good experiments, and no doubt is felt about their approximate accuracy.   As will be seen from the Table, they fit in very well with the calculated mobilities for ions consisting of 4 and 7 water-molecules respectively.   This suggests that these ions are formed by the union of a water-molecule which has lost an electron, to groups of 3 and 6 water-molecules.   It is possible that all the positive ions are formed in this way, that is, by the union of a positively charged molecule with a stable or semi-stable group of water-molecules which is already in existence.   When the number of molecules becomes considerable, the resulting ion has practically the same mobility as the negative ion, which is formed from a similar group by the adding on of an electron.

All the ions observed have now been accounted for with the exception of the negative ion 4·42.   There are only two observations of this ion, so that the exact value of its mobility is not very well established.   The best explanation then that can be given is that it consists of 5 water-molecules; such an ion would have a mobility about 4·15, as compared with the observed value of 4·42.

It is worthy of note that it is just those ions which show up most consistently and easily on the experimental curves which fall most readily into a regular classification.   These are the very fast ions and the ions with mobilities from 1·97 to 1·04 inclusive.   We cannot so easily classify the others, partly because of an uncertainty as to their accurate mobility values, and partly, no doubt, because some of them represent aggregates of a small degree of stability which are not easily made to show a relationship with what we may regard as the more definite or stable forms.

On the supposition then that the ions are composed of various numbers of water-molecules we have been able to show that if the ions are built up in a certain regular way the observed mobilities agree fairly well with a theoretical estimate from the elastic collision point of view.   The agreement is better the greater the number of molecules in the ion, and for the last six ions the agreement is extremely good.   Then the last ion is found to consist of 54 water-molecules (assuming a regular step of 6 or a multiple of 6), agreeing as well as could be expected with our previous estimate of 66 to 71.

Possibility that the Ions are Groups of Air-Molecules.

It might be argued, however, that a set of ions could be built up from air-molecules which would fit the observed values as well as our theoretical water-ions. But the previous work on the large ions has led to the idea that the slowest of the present ions (mobility 1·06) is altogether water. We would have to suppose, then, that as the ions became smaller a certain proportion of air-molecules entered into their composition, and that finally at a certain small size they were altogether composed of air-molecules. But the very good agreement between the calculated and theoretical values for the last six ions suggests that they at least are altogether water. There is nothing to suggest a change in composition. Assuming that aggregations of air-molecules are possible, we can calculate the mobilities which ions composed of various small numbers of air-molecules should have. Using Sir J. J. Thomson's formula as before, we find that ions containing 1, 2, 3, 4, 5 and 6 air-molecules would have mobilities 12, 8·05, 6·4, 5·47, 4·85 and 4·43. The first of these numbers (12) is practically the same as the mobility calculated for a water-molecule, and indeed the two following, 8·05 and 6·4, are not far removed from the corresponding values for water, 7·4 and 5·66. If we consider the ratios of the mobilities of the first three ions we find that the observed numbers are as 100 : 55 : 40. The values calculated for water are as 100 : 60 : 46, while those for air are as 100 : 67 : 53. The observed numbers, therefore, agree better with the supposition that the ions are composed of water than with the idea that they are composed of air. The explanation of the two positive ions which do not correspond to any negative ions fits in very well on the supposition that the ions are of water. If the ions are composed of air-molecules it is hard to see why there should be any difference between positive and negative, because the ion will then consist of a cluster of molecules owing whatever stability it has to its charge. The number of molecules in such an ion would depend only on the charge. We cannot imagine a cluster of gaseous molecules becoming an ion by picking up an electron or a positive molecule, because there is no evidence that such clusters exist in a gas like oxygen or nitrogen. In fact the only evidence of the existence of such uncharged clusters is in the case of moist gases, where everything points to these clusters being composed of water. We cannot, of course, exclude the possibility that the first ion (mobility 15·2) may be a molecule of oxygen or nitrogen, because the observed value would agree as well with that assumption as with the supposition that it is a molecule of water.

Identity of Some of the Water Ions with Ordinary Gaseous Ions.

If we consider the four ions, the observed mobilities of which are (for negative ions) 1·94, 1·70, 1·49 and 1·34, we find indications of a possible connection with the mobilities of ordinary ions produced by X-rays or other ionising agents in air under different conditions.   For example, in saturated air the ordinary values* for mobility of negative and positive ions are respectively 1·51 and 1·37, corresponding approximately to the third and fourth of the ions above.   For dry air the values given by different observers vary a great deal, and there is good reason for believing that this should be attributed to the degree of drying arrived at in various cases.   For example, Wellisch† gives the values 1·78 and 1·54 for negative and positive. Langevin's‡ values are 1·70 and 1·40.   In more recent work, where a very high degree of dryness was attained, Wellisch§ finds the values 1·93 and 1·23, corresponding to some extent with Zeleny's‖ values 1·87 and 1·36. All these values can be grouped fairly well into four classes corresponding to the four values quoted above, the negative ion having values approximating to 1·94, 1·70, or 1·49, according to the dryness of the air, and the positive ion having values approximating to 1·49 or 1·34 in the same way, with a tendency towards the last value occurring more frequently.   The small ion in air, therefore, must at the very least resemble closely in mass and size the water-ions which we have been observing.   The way in which its mobility decreases in damp air resembles exactly the way in which the water-ion adds on further groups of water-molecules.   The view is put forward in this paper that the ordinary small ion is composed of water, the negative ion being an aggregate of 18, 24, or 30 molecules of water, according to the condition of the air as regards humidity, and the positive ion consisting of 30 or 36 water-molecules, more often the latter number.   Of course we cannot insist on the exact accuracy of the number of water-molecules assigned, but it is felt that they are fairly close to the true values.   This theory of the nature of the small ions applies to any of the permanent gases as well as to air. The nature of the small ion in a readily condensable gas is probably different.   The justification of the theory that the small ion is composed of water is found in the ease with which it explains several of the well-known properties of the gaseous ion.

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* Zeleny, 'Phil. Trans.,' 1900.

† Wellisch, 'Phil Trans.,' 1909.

‡ Langevin, 'Annales de Chimie et de Physique,' 1903.

§ Wellisch, 'American Journal of Science,' May, 1915.

‖ Zeleny, *loc. cit.*

The Mobility of the Ion in Different Gases.

In a number of the permanent gases the mobility of the ion is inversely proportional to the square root of the density. This result follows immediately from our theory, for, the mass of the ion being large compared with that of the gas-molecule, the formula of Sir J. J. Thomson, which we have been using, becomes

$$R = \text{constant}/\sqrt{M_2},$$

M_2 being the mass of the gas-molecule.

We can, moreover, use the full formula to calculate the mobilities of ions having the composition that we assume in different gases. For example, taking Sutherland's value for the molecular diameter of hydrogen, we can calculate the mobilities of ions composed of 18, 24, 30, and 36 water-molecules in hydrogen.

Table VI.—Hydrogen.

Composition of ion.	Calculated mobility.	Observed values.				
		Moist gas (Zeleny).*	Dry gas.			
			Zeleny.*	Chattock.†	Franck and Pohl.‡	Haines.§
18 H$_2$O mol.	7·93	—	−7·95	−7·43	−7·68	−7·9
24 ,,	6·81	—	+6·70	—	—	—
30 ,,	6·00	−5·6	—	—	+6·02	—
36 ,,	5·44	+5·3	—	+5·4	—	+5·4

The agreement between mobilities calculated by this method and the values observed is extremely good. Again, as in the case of air, we find the negative charge associated with 18 water-molecules, and the positive charge associated with 36, when the drying is specially good. Under other conditions of moisture the other two sizes tend to appear.

Space will not permit of the extension of these calculations to the other gases. It may be said, however, that the agreement is good in the case of the more permanent gases, but not so good in the case of gases which are easily condensable.

The further advantages of the theory of the small ion just put forward may be summarised rapidly as follows :—

* Zeleny, *loc. cit.*
† Chattock, 'Phil. Mag.,' 1899.
‡ Franck and Pohl, 'Verh. d. Deut. Phys. Ges.,' 1907.
§ Haines, 'Phil. Mag.,' April, 1916.

(1) It permits of ready explanation of the results of Blanc* and Wellisch†
for the mobilities of ions in gaseous mixtures.

(2) It can be harmonised with Phillips'‡ results on the variation of
mobility with temperature.

(3) The sizes attributed to the ions are in fair agreement with the sizes
deduced from the coefficient of diffusion.

(4) The abnormally high mobilities observed by Haines§ in very pure
hydrogen are readily explained if we assume that the "impurity" necessary
for the formation of ions is water, and that the ions which successively
appear are composed of 1, 6, 18, and 36 water-molecules respectively.

CONCLUSION.

It is no part of the theory given in this paper to insist on the absolute
values (18, 36, etc.) of the numbers of molecules supposed to constitute each
ion. These are the numbers which fit in best with our present knowledge of
molecular sizes. With fuller information, the ions might be better repre-
sented in terms of some other unit rather than 6.|| But enough evidence
has been given to show that, in the case of ions produced by spraying water,
there is a regular building up of aggregates of water, and that certain of
these aggregates, which seem to be specially stable, are at the very least
similar, and are probably identical with the small ions observed in various
gases.

It is clear that there are many ways in which the ideas put forward in
this paper can be experimentally tested. Further work should render it
possible to decide whether the larger ions are to be regarded as loose
groupings or compact aggregates. It should be possible also to obtain more
information on the more important question of the nature of the ordinary
small ion, and to test the theory put forward in this paper.

* Blanc, 'Journ. de Phys.,' vol. 7, p. 838 (1908).
† Wellisch, 'Roy. Soc. Proc.,' vol. 82, p. 500 (1909).
‡ Phillips, 'Roy. Soc. Proc.,' vol. 78 (1907).
§ Haines, 'Phil. Mag.,' April, 1916.
|| Perhaps in this connection the structure of crystallised water is not without
significance. As is well known, snow crystals are almost always flat and hexagonal
in character, taking various forms such as that of a six-pointed star, but showing
evidence of having been formed around a single nucleus and having characteristic angles
of 60° and 120°.